

FORM PTO-1390 (Modified)
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U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

TRANSMITTAL LETTER TO THE UNITED STATES

218059US0PCT

DESIGNATED/ELECTED OFFICE (DO/EO/US)

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR

CONCERNING A FILING UNDER 35 U.S.C. 371

10/030430

INTERNATIONAL APPLICATION NO.

INTERNATIONAL FILING DATE

PRIORITY DATE CLAIMED

PCT/JP00/04623

11 JULY 2000

12 JULY 1999 (EARLIEST)

TITLE OF INVENTION

CHEMICALLY AMPLIFIED RESIST COMPOSITION

APPLICANT(S) FOR DO/EO/US

Tadayuki FUJIWARA, et al.

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (24) indicated below.
4. ☒ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
 - a. ☐ is attached hereto (required only if not communicated by the International Bureau).
 - b. ☒ has been communicated by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
 - a. ☒ is attached hereto.
 - b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
 - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
 - b. ☐ have been communicated by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☒ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
10. ☐ An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).
11. ☒ A copy of the International Preliminary Examination Report (PCT/IPEA/409).
12. ☒ A copy of the International Search Report (PCT/ISA/210).

Items 13 to 20 below concern document(s) or information included:

13. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☐ A **FIRST** preliminary amendment.
16. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
17. ☐ A substitute specification.
18. ☐ A change of power of attorney and/or address letter.
19. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
20. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
21. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
22. ☐ Certificate of Mailing by Express Mail
23. ☒ Other items or information:

Notice of Priority / PCT/IB/304 / PCT/IB/308
PTO-1449

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR 1.01) 10/030430		INTERNATIONAL APPLICATION NO. PCT/JP00/04623		ATTORNEY'S DOCKET NUMBER 218059US0PCT	
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24. The following fees are submitted:

BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :				CALCULATIONS PTO USE ONLY	
<input type="checkbox"/> Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO	\$1040.00				
<input checked="" type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO	\$890.00				
<input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO	\$740.00				
<input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4)	\$710.00				
<input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4)	\$100.00				
ENTER APPROPRIATE BASIC FEE AMOUNT =		\$890.00			
Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492 (e)).				\$0.00	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	17 - 20 =	0	x \$18.00	\$0.00	
Independent claims	3 - 3 =	0	x \$84.00	\$0.00	
Multiple Dependent Claims (check if applicable).				<input checked="" type="checkbox"/>	\$280.00
TOTAL OF ABOVE CALCULATIONS =				\$1,170.00	
<input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2.				\$0.00	
SUBTOTAL =				\$1,170.00	
Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492 (f)).				\$0.00	
TOTAL NATIONAL FEE =				\$1,170.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable).				<input type="checkbox"/>	\$0.00
TOTAL FEES ENCLOSED =				\$1,170.00	
				Amount to be refunded	\$
				charged	\$

a. ☒ A check in the amount of **\$1,170.00** to cover the above fees is enclosed.


b. ☐ Please charge my Deposit Account No. _____ in the amount of _____ to cover the above fees. A duplicate copy of this sheet is enclosed.

c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. **15-0030**. A duplicate copy of this sheet is enclosed.

d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. **Credit card information should not be included on this form.** Provide credit card information and authorization on PTO-2038.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.


SEND ALL CORRESPONDENCE TO:



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 SIGNATURE
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 REGISTRATION NUMBER
 Jan. 10, 2002
 DATE

CHEMICALLY AMPLIFIED RESIST COMPOSITION

TECHNICAL FIELD

The present invention relates to a chemically
5 amplified resist composition, particularly a
chemically amplified resist composition suitably used
in microfabrication using an excimer laser beam or an
electron beam.

10 BACKGROUND ART

In recent years, in the microfabrication
employed in production of a semiconductor device or a
liquid crystal device, a progress has been seen in
lithography technology; as a result, a rapid progress
15 is taking place in fine pattern formation. As the
means for fine pattern formation, a light of shorter
wavelength is generally used for exposure;
specifically, a conventional ultraviolet light
represented by g-line or i-line is being changed to a
20 DUV.

Currently, a lithography technology using a KrF
excimer laser beam (248 nm) has been introduced into
the market; a lithography technology using an ArF
excimer laser beam (193 nm) of even shorter
25 wavelength is being introduced; and a lithography

technology using a F_2 excimer laser beam (157 nm) is under study as a next generation technology. Further, vigorous studies are under way on lithography technologies using an electron beam, an EUV, an X ray, an ion beam, etc., which are slightly different from the above technologies.

As a resist giving a high resolution to a light source of short wavelength or to an electron beam, an EUV, an X ray, an ion beam or the like, there was proposed "a chemically amplified resist" by IBM Co. Currently, improvements for this chemically amplified resist and developments of a new chemically amplified resist are being made actively.

Use of a light source of shorter wavelength has forced the structural change of the resin used in a resist. Therefore, in a lithography using a KrF excimer laser beam, there is used a polyhydroxystyrene showing high transparency to 248 nm, or a resin obtained by protecting the hydroxyl group of the polyhydroxystyrene with an acid-dissociable, dissolution-inhibiting group; in a lithography using an ArF excimer laser beam, attention is being paid to an acrylic resin transparent to 193 nm or a cycloolefin resin because the polyhydroxystyrene has insufficient transparency

to 193 nm and is substantially unusable.

As the acrylic resin, there are mentioned those disclosed in JP-A 39665/92, JP-A 207069/98, etc.; as the cycloolefin resin, there are mentioned those disclosed in JP-A 153864/98, etc.

These resins, however, are still insufficient in performance, and a higher resolution and a good resist shape are needed. As the reason for low resolution and inferior resist shape, there is pointed out, for example, the deactivation of acid caused by the basic substance in air or the basic substance infiltrating from substrate. As a method for solving such a problem, it is known, for example, to add a basic compound in a KrF excimer laser beam lithography (JP-A 179300/97).

Currently, however, a resist of higher performance is required in industry. In an ArF laser beam lithography, in particular, a particular light source (wavelength) and a particular resin are used and a particular resolution is required; therefore, no effective additive has been found.

DISCLOSURE OF THE INVENTION

In view of the above situation, the present invention aims at providing a chemically amplified

resist composition which is high in sensitivity and resolution and capable of giving a good resist shape when used in a DUV excimer laser beam lithography or a lithography using an electron beam, an EUV, an X ray, an ion beam or the like.

In order to achieve the above aim, the present invention provides a chemically amplified resist composition comprising:

a resin which becomes soluble in an aqueous alkali solution in the presence of an acid, a photo acid generator, and an amine derivative which shows, in water of 25°C, such a basicity as to form a conjugate acid and has a medium polarity.

This chemically amplified resist composition is high in sensitivity and resolution and good in resist shape and can form a very precise and fine resist pattern stably.

Therefore, the present chemically amplified resist composition can be suitably used in a DUV excimer laser beam lithography or a lithography using an electron beam, an EUV, an X ray, an ion beam or the like, particularly in a lithography using an ArF excimer laser beam.

BEST MODE FOR CARRYING OUT THE INVENTION

The present invention is described in detail below.

It is already known to add a basic compound to
5 a chemically amplified resist. Such a basic compound is generally called a quencher because the compound is considered to quench an acid generated from a photo acid generator.

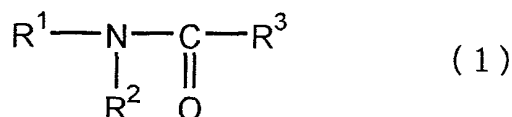
The action mechanism of the quencher is not
10 clear. However, as to the mechanism, there is, for example, a theory that the quencher forms an acid-base equilibrium in a resist system and supplies a fresh acid to a portion of reduced acid concentration. However, the true action mechanism of the quencher is
15 presumed to be very complicated because various factors such as compatibility with resin, diffusion and the like are also involved.

It is known that by adding this quencher to a resist, various favorable effects are obtained, for
20 example, formation of a sparingly soluble surface layer is prevented, a higher resolution is obtained, and higher PED stability is obtained.

The present inventors found out that by adding, as a quencher, an amine derivative having at least
25 one of the three characteristics explained below, a

chemically amplified resist is obtained which is significantly improved in resolution and gives a very good resist shape.

The first characteristic of the amine derivative used in the present invention lies in its skeleton. That is, the amine derivative of the present invention is preferably an amide compound represented by the following general formula (1):



(wherein R^1 , R^2 and R^3 are each independently hydrogen or an alkyl group having 1 to 30 carbon atoms).

At least two of R^1 , R^2 and R^3 in the general formula (1) preferably bond to each other to form a cyclic skeleton because there are obtained advantages such as very high resolution, good resist shape and the like.

Also, at least one of R^1 and R^2 in the general formula (1) is preferably a cyclic alkyl group having 3 to 30 carbon atoms, for the same reasons.

As specific examples of the amide compound of the general formula (1), there can be mentioned N-cyclohexylformamide, N-cyclohexylacetamide, 1-cyclohexyl-2-pyrrolidinone, N-cyclohexyl- δ -valerolactam, N-cyclohexyl- ϵ -caprolactam, N-

isobornylformamide, N-isobornylacetamide, N-isobornyl-2-pyrrolidinone, N-isobornyl- δ -valerolactam, N-isobornyl- ϵ -caprolactam, N-adamantylformamide, N-adamantylacetamide, N-adamantyl-2-pyrrolidinone, N-adamantyl- δ -valerolactam, N-adamantyl- ϵ -caprolactam, N-tricyclodecanylformamide, N-tricyclodecanylacetamide, N-tricyclodecanyl-2-pyrrolidinone, N-tricyclodecanyl- δ -valerolactam, N-tricyclodecanyl- ϵ -caprolactam, N-dicyclopentadienylformamide, N-dicyclopentadienylacetamide, N-dicyclopentadienyl-2-pyrrolidinone, N-dicyclopentadienyl- δ -valerolactam, and N-dicyclopentadienyl- ϵ -caprolactam.

The amide compound represented by the general formula (1) can be used in one kind or in admixture of two or more kinds.

The content of the amide compound represented by the general formula (1) varies depending upon the kind of the amide compound but is ordinarily 0.01 to 10 moles, preferably 0.05 to 1 mole per mole of the photo acid generator.

When the content of the amide compound represented by the formula (1) is higher in the ordinary content range, a better resist shape is obtained generally; when the content is lower, higher

resist sensitivity and higher developability of exposed resist portion are obtained generally.

The second characteristic of the amine derivative used in the present invention lies in the intensity of the basicity. That is, the amine derivative is preferably a basic compound capable of forming a conjugate acid in water of 25°C.

Incidentally, the basicity of the basic compound can be quantified by the pKa of the conjugate acid generated by the basic compound. In the present invention, the pKa of the conjugate acid in water of 25°C is preferably -3 to 3, more preferably -2 to 2.

By using, as a quencher, a basic compound capable of generating a conjugate acid having a pKa of -3 to 3, in a resist composition, formation of a sparingly soluble surface layer is prevented and an improved resolution is obtained, in particular.

Effects such as improved PED stability and the like are also obtained, and a resolution far higher than in using a conventional quencher is obtained.

When a basic compound forming a conjugated acid having a pKa of less than -3 is used, an inferior resist shape may result; when the pKa of conjugate acid is more than 3, resist sensitivity or

developability of exposed resist portion may be low.

The basic compound capable of forming a conjugate acid having a pKa of -3 to 3 can be used in one kind or in combination of two or more kinds, so
5 as to meet the necessity.

As the basic compound capable of forming a conjugate acid having a pKa of -3 to 3, used in the present invention, there can be mentioned, for example, acetamide, acetamidine, 3-aminopyridine-1-
10 oxide, 4-benzylpyridine-1-oxide, betaine, 2-bromoaniline, 2-bromopyridine, 2-chloro-6-nitroaniline, 4-chloro-2-nitroaniline, 2-chloropyridine, 3-chloropyridine, 3-chloro-o-toluidine, colchicine, 2-cyanopyridine, 3-
15 cyanopyridine, 4-cyanopyridine, 3,5-dibromoaniline, 3,5-chloroaniline, 2,5-dichloro-4-nitroaniline, 3,5-diiodoaniline, 4-dimethylaminozenzaldehyde, 2,4-dimethylpyridine-1-oxide, 3,5-dinitroaniline, 5-ethyl-2-methylpyridine-1-oxide, 2-ethylpyridine-1-
20 oxide, 3-ethylpyridine-1-oxide, 2-fluoropyridine, 3-fluoropyridine, 2-iodoaniline, 2-iodopyridine, isocreatine, 2-methoxycarbonylaniline, 4-methoxycarbonylaniline, 2-methoxycarbonylpyridine, 2-(N-methylbenzamido)pyridine, 2-(N-
25 methylmethanesulfonamido)pyridine, 2-methylpyridine-

1-oxide, 3-methylpyridine-1-oxide, 4-methylpyridine-
 1-oxide, 3-methylsulfonylaniline, 4-
 methylsulfonylaniline, 2-nitroaniline, 3-nitroaniline,
 4-nitroaniline, phenazine, 5-phenylbarbituric acid,
 5 pyrazine, pyrazinecarboxamide, pyrazole, pyridazine,
 3-pyridinecarbonitrile, pyridine-1-oxide, pyrimidine,
 3-pyrroline, quinoxaline, 2,3,5,6-tetramethyl-4-
 methylaminopyridine, triazoline, thiourea, 4-
 (trifluoromethyl)aniline, 2,4,6-trimethylpyridine-1-
 10 oxide, diphenylamine, 2-chloroaniline, 2-
 acetylpyridine, N-isopropylmethacrylamide, N-
 acetylethanolamine, β -propiolactam, 2-pyrrolidinone,
 δ -valerolactam, ϵ -caprolactam, benzamide, N-
 methylbenzamide, N-ethylbenzamide, N-
 15 isopropylbenzamide, N-isobutylbenzamide, N-sec-
 butylbenzamide, N-tert-butylbenzamide, N-
 benzylbenzamide, N,N-dimethylbenzamide, N,N-
 diethylbenzamide, N,N-diisopropylbenzamide,
 benzoylpiperidine, 2-azacyclooctanone, 2-
 20 azacyclononanone, N-methylacetamide, N-ethylacetamide,
 N-tert-butylacetamide, N-benzylacetamide, N-p-
 methoxybenzylacetamide, N-p-chlorobenzylacetamide,
 N,N-diethylacetamide, N,N-dimethylacetamide, urea,
 N,N-dimethylformamide, N-cyclohexylformamide, and N-
 25 isopropylacrylamide.

Of these, preferred are (meth)acrylamides, acetamides, isobutyramides, formamides and lactams.

The use amount of the basic compound capable of forming a conjugate acid having a pKa of -3 to 3 is
5 appropriately determined depending upon the kind of the basic compound, but is ordinarily 0.01 to 10 moles, preferably 0.05 to 1 mole per mole of the photo acid generator.

When the use amount of the basic compound
10 capable of forming a conjugate acid having a pKa of -3 to 3 is larger, a better resist shape is obtained generally; when the amount is smaller, higher resist sensitivity and higher developability of exposed resist portion are obtained generally.

15 The third characteristic of the amine derivative used in the present invention lies in the polarity. That is, the amine derivative is preferably a basic compound which has neither excessively high polarity nor excessively low
20 polarity and has a medium polarity.

Incidentally, the polarity of the basic compound can be quantified by the water-octanol partition coefficient (Log P). In the present invention, the water-octanol partition coefficient
25 (Log P) at 25°C is preferably 0 to 1.5.

The water-octanol partition coefficient (Log P) referred to herein can be determined by a formula of a structure activity relationship described in J. Computational Chem., Vol. 9, No. 1, pp. 80 to 90(1988). Specifically, the water-octanol partition coefficient (Log P) of a basic compound can be determined from the above formula of the structure activity relationship by optimizing a molecular structure of the compound in its energy level using a nonempirical molecular orbital method (RHF/STO-3G) and a semiempirical molecular orbital method (AMI or PM3).

A smaller water-octanol partition coefficient (Log P) indicates more amount distribution in water and a larger water-octanol partition coefficient indicates more amount distribution in octanol.

By using, as a quencher, a basic compound having a water-octanol partition coefficient (Log P) of 0 to 1.5, in a resist composition, formation of a sparingly soluble surface layer is prevented and an improved resolution is obtained, in particular.

Effects such as improved PED stability and the like are also obtained, and a resolution far higher than in using a conventional quencher is obtained.

When a basic compound having a water-octanol

partition coefficient (Log P) of less than 0 is used,
a inferior resist shape may result; when the water-
octanol partition coefficient (Log P) is more than
1.5, resist sensitivity or developability of exposed
5 resist portion may be low.

The basic compound having a water-octanol
partition coefficient (Log P) of 0 to 1.5 can be used
in one kind or in combination of two or more kinds,
so as to meet the necessity.

10 As the basic compound having a water-octanol
partition coefficient (Log P) of 0 to 1.5, used in
the present invention, there can be mentioned, for
example, N-isopropylmethacrylamide, N-
cyclohexylformamide, 1-cyclohexyl-2-pyrrolidinone,
15 ϵ -caprolactam, N-adamantylacetamide, N-
isopropylisobutyramide, 1-acetyl-3-methylpiperizine,
N-isopropylacrylamide, N-vinylcaprolactam, N-
vinylpyrrolidinone, dimethylaminoethyl methacrylate,
N,N-diethylacrylamide,
20 dimethylaminopropylmethacrylamide, and
dimethylaminopropylacrylamide.

Of these, preferred are (meth)acrylamides,
acetamides, isobutyramides, formamides and lactams.

The use amount of the basic compound having a
25 water-octanol partition coefficient (Log P) of 0 to

1.5 is appropriately determined depending upon the kind of the basic compound, but is ordinarily 0.01 to 10 moles, preferably 0.05 to 1 mole per mole of the photo acid generator.

5 When the use amount of the basic compound having a water-octanol partition coefficient (Log P) of 0 to 1.5 is larger, a better resist shape is obtained generally; when the amount is smaller, higher resist sensitivity and higher developability
10 of exposed resist portion are obtained generally.

 As described above, the amine derivative used in the present invention as a quencher, preferably has at least one of the first characteristic regarding the skeleton, the second characteristic
15 regarding the basicity and the third characteristic regarding the polarity.

 Of such amine derivatives, those which have been confirmed to be particularly preferably used in the present invention, include N-
20 isopropylmethacrylamide, N-cyclohexylformamide, 1-cyclohexyl-2-pyrrolidinone, N-methylacetamide, ϵ -caprolactam, 1-acetyl-3-methylpiperizine, etc.

 According to the study hitherto made by the present inventors, amine derivatives having two of
25 the above three characteristics are generally

preferred, and amine derivatives having all of the three characteristics are generally more preferred.

Such an amine derivative is used in an amount of preferably 0.01 to 10 moles, more preferably 0.05
5 to 1 mole per mole of the photo acid generator.

At least one kind of amine derivative having at least one of the three characteristic can be used so as to meet the necessity. When two or more kinds are used, the total amount of the kinds used is
10 preferably within the above range.

Next, description is made on the resin which becomes soluble in an aqueous alkali solution in the presence of an acid, contained in the chemically amplified resist composition of the present invention
15 (this resin is hereinafter described simply as resin, in some cases). There is no particular restriction as to this resin as long as it becomes soluble in an aqueous alkali solution in the presence of an acid, and the resin may be any resin for chemically
20 amplified resist composition. The resin is appropriately selected depending upon the light source used in lithography.

For example, when the light source is a KrF excimer laser beam or an electron beam, a resin of
25 high etching resistance obtained by (co)polymerizing

p-hydroxystyrene or its derivative is used suitably.
As a matter of course, such a resin contains, in the
(co)polymer structure, functional group which is
eliminated by an acid and becomes soluble in an
5 alkaline developing solution.

Preferred specific examples of such a
(co)polymer are those obtained by protecting the
hydroxyl group of p-hydroxystyrene monomer units or
the carboxyl group of other monomer units with
10 acetoxy group, tert-butyl group, tetrahydropyranyl
group, methyladamantyl group or the like.

When the light source is an ArF excimer laser
beam, the above-mentioned resin is unusable because
the wavelength of the light source is short and the
15 resin's light transmission is low. Therefore, there
is suitably used a resin having an alicyclic skeleton,
which has a high light transmission and relatively
high etching resistance.

As specific examples of such a resin, there can
20 be mentioned an acrylic resin described in JP-A
090637/97 and JP-A 207069/98 and an olefinic resin
described in JP-A 207070/98 and JP-A 218941/98.

However, when the amide compound and the basic
compound both disclosed in the present invention are
25 used as a quencher, there is preferred a resin

containing monomer units having an alicyclic skeleton and monomer units having a lactone skeleton, or a cycloolefin resin, and there are particularly preferred a polymer containing (meth)acrylic acid ester monomer units having an alicyclic skeleton and (meth)acrylic acid ester monomer units having a lactone skeleton.

The monomer units having an alicyclic skeleton can impart transparency and high resistance to dry etching, to the resin and a resin composition thereof. In particular, those monomer units containing acid-eliminatable protective group (the alicyclic group per se may be such a protective group) can impart high sensitivity at 193 nm.

Preferred as the monomer units having an alicyclic skeleton is a (meth)acrylic acid ester containing an alicyclic skeleton in the ester moiety.

In particular, the (meth)acrylic acid ester monomer units having an alicyclic skeleton is preferably selected from the group consisting of cyclohexyl (meth)acrylate, isobornyl (meth)acrylate, adamantyl (meth)acrylate, tricyclodecanyl (meth)acrylate, dicyclopentadienyl (meth)acrylate, and their derivatives formed by introducing a substituent such as alkyl group, carboxyl group,

hydroxyl group or the like, onto the alicyclic ring of each of the above monomer units.

Specifically, there can be mentioned 1-isobornyl methacrylate, 2-methacryloyloxy-2-methyladamantane, cyclohexyl methacrylate, adamantyl methacrylate, tricyclodecanyl methacrylate, dicyclopentadienyl methacrylate, etc.

These monomer units having an alicyclic skeleton can be used singly or, as necessary, in combination of two or more kinds.

The (meth)acrylic acid ester monomer units having a lactone skeleton can impart adhesivity to substrate, to the resin and a resin composition thereof. In particular, those monomer units containing acid-eliminatable protective group (the lactone group per se may be such a protective group) can impart high sensitivity at 193 nm.

Preferred as the monomer units having a lactone skeleton is a (meth)acrylic acid ester containing a lactone skeleton in the ester moiety.

In particular, the (meth)acrylic acid ester monomer units having a lactone skeleton is preferably selected from the group consisting of (meth)acrylates having a δ -valerolactone ring, (meth)acrylates having a γ -butyrolactone ring, and their derivatives

formed by introducing a substituent such as alkyl group, carboxyl group, hydroxyl group or the like, onto the lactone ring of each of the above monomer units.

- 5 Specifically, there can be mentioned β -methacryloyloxy- β -methyl- δ -valerolactone, β -methacryloyloxy- γ -butyrolactone, β -methacryloyloxy- β -methyl- γ -butyrolactone, α -methacryloyloxy- γ -butyrolactone, 2-(1-methacryloyloxy)ethyl-4-
- 10 butanolide, pantolactone methacrylate, etc.

These monomer units having an alicyclic skeleton can be used singly or, as necessary, in combination of two or more kinds.

- The resin which becomes soluble in an aqueous
- 15 alkali solution in the presence of an acid, used in the present invention, has no particular restriction as to the weight-average molecular weight. The weight-average molecular weight, however, is preferably 1,000 or more in view of the dry etching
- 20 resistance and resist shape required and 100,000 or less in view of the solubility in resist solvent and resolution required.

- The resin which becomes soluble in an aqueous alkali solution in the presence of an acid, has no
- 25 particular restriction, either, as to the production

process. However, there can be mentioned, as a preferred production process, for example, a so-called dropping polymerization process which comprises dissolving monomers and a polymerization
5 initiator in an organic solvent and dropping the resulting solution in an organic solvent kept at a given temperature.

The organic solvent used in this dropping polymerization process is preferably a solvent
10 capable of dissolving all of the monomers mixture, the polymerization initiator and the copolymer obtained. There can be mentioned, for example, 1,4-dioxane, isopropyl alcohol, acetone, tetrahydrofuran, methyl isobutyl ketone.

15 As the polymerization initiator used in the dropping polymerization process, there can be mentioned, for example, azo compounds such as azobisisobutyronitrile, 2,2'-azobis(2,4-dimethylvaleronitrile) and the like; and organic
20 peroxides such as benzoyl peroxide and the like. A mercaptan such as n-butylmercaptan, n-octylmercaptan or the like may be used as a chain transfer agent, in combination with the polymerization initiator.

In the dropping polymerization, the
25 polymerization temperature is preferably 50 to 150°C,

and the dropping time is preferably 6 hours or more. After the completion of the dropping, the polymerization temperature is preferably kept for about 2 hours to complete polymerization.

5 Next, the copolymer solution obtained is diluted to an appropriate solution viscosity using a good solvent such as tetrahydrofuran, 1,4-dioxane or the like; then, the diluted solution is dropped into
10 a large amount of a poor solvent such as methanol, water or the like to give rise to precipitation. The resulting precipitate is collected by filtration and dried sufficiently, whereby a resin used in the present invention can be obtained. This
15 reprecipitation step is unnecessary in some cases but is very effective to remove the unreacted monomers, polymerization initiator, etc. remaining in the polymerization solution. The unreacted monomers, when remaining as they are, may adversely affect the properties of the resist to be compounded later;
20 therefore, it is preferred to remove them.

 The thus obtained resin is dissolved in a solvent together with a photo acid generator, whereby a chemically amplified resist composition (a solution) can be obtained.

25 The photo acid generator used above has no

particular restriction as to the kind and can be freely selected from those usable as such an agent for chemically amplified resist composition.

Specifically, there can be mentioned onium salt
5 compounds, sulfonimide compounds, sulfone compounds, sulfonic acid ester compounds, quinone diazide compounds, diazomethane compounds, etc.

Of these, onium salt compounds are preferred, and there can be mentioned, for example, sulfonium
10 salts, iodonium salts, phosphonium salts, diazonium salts and pyridinium salts.

As specific examples, there can be mentioned triphenylsulfonium triflate, triphenylsulfonium hexafluoroantimonate, triphenylsulfonium
15 naphthalenesulfonate, (hydroxyphenyl)benzylmethylsulfonium toluenesulfonate, diphenyliodonium triflate, diphenyliodonium pyrenesulfonate, diphenyliodonium dodecylbenzenesulfonate, and diphenyliodonium
20 hexafluoroantimonate.

The photo acid generator can be used in one kind or in admixture of two or more kinds.

The amount of the photo acid generator used is appropriately determined depending upon the kind of
25 the photo acid generator used. However, the amount

is ordinarily 0.1 to 20 parts by mass, particularly preferably 0.5 to 10 parts by mass per 100 parts by mass of the resin. When the amount of the photo acid generator used is less than 0.1 part by mass, it may
5 be difficult to sufficiently give rise to the chemical reaction caused by the catalysis of the acid generated when the agent is irradiated with a light. When the amount is more than 20 parts by mass, unevenness may appear in coating of resist
10 composition and scum, etc. may be formed during development.

The solvent used is selected appropriately depending upon the application of resist composition. Preferably, the solvent is selected in view of the
15 solubility of produced copolymer and photo acid generator, and other factors such as uniformity and appearance of formed film, safety and the like.

As solvents satisfying these requirements, there can be mentioned, for example, straight chain
20 ketones such as 2-pentanone, 2-hexanone and the like; cyclic ketones such as cyclopentanone, cyclohexanone and the like; propylene glycol monoalkyl ether acetates such as propylene glycol monomethyl ether acetate, propylene glycol monoethyl ether acetate and
25 the like; ethylene glycol monoalkyl ether acetates

such as ethylene glycol monomethyl ether acetate,
ethylene glycol monoethyl ether acetate and the like;
propylene glycol monoalkyl ethers such as propylene
glycol monomethyl ether, propylene glycol monoethyl
5 ether and the like; ethylene glycol monoalkyl ethers
such as ethylene glycol monomethyl ether, ethylene
glycol monoethyl ether and the like; diethylene
glycol alkyl ethers such as diethylene glycol
dimethyl ether, diethylene glycol diethyl ether and
10 the like; esters such as ethyl acetate, ethyl lactate
and the like; alcohols such as cyclohexanol, 1-
octanol and the like; ethylene carbonate; and γ -
butyrolactone. These solvents can be used singly or
in admixture of two or more kinds.

15 The resist composition (solution) may further
contain, as necessary, various additives such as
surfactant, sensitizer, halation inhibitor, storage
stabilizer, antifoaming agent and the like.

As examples of the surfactant, there can be
20 mentioned nonionic surfactants such as
polyoxyethylene lauryl ether, polyethylene glycol
dilaurate and the like; and commercial products such
as Polyflow No. 75 (a product of Kyoeisha chemical
Co., Ltd.), Megaface F 173 (a product of Dainippon
25 Ink and Chemicals, Incorporated), Surflon SC-105 (a

product of Asahi Glass Co., Ltd.), L-70001 (a product of Shin-Etsu Chemical Co., Ltd.) and the like.

In forming a resist pattern using the thus-obtained resist composition (solution), the solution
5 is coated on a substrate in a give thickness by a known means such as spin coating or the like, then dried appropriately, and irradiated using a given light source. Thereafter, baking is conducted as necessary, followed by development using an alkali
10 developing solution to obtain an intended pattern.

The above-described chemically amplified resist composition has a very high resolution.

Specifically, the chemically amplified resist composition can have a resolution of 0.15 micron or
15 less, preferably 0.14 micron or less, more preferably 0.13 micron or less, most preferably 0.12 micron or less; when the resist composition is coated on bare silicon to form a resist of 0.5 micron in thickness, a light of 193 nm emitted from an argon fluorine
20 excimer laser is applied to the resist at an exposure of 5 mJ/cm² or less through a mask having a pattern of line/space = 1/1 to project the pattern to the resist in 1/4 reduction, and the resulting resist is heat-treated at 120°C for 60 seconds and subjected to
25 development with a 2.38 mass % aqueous

tetramethylammonium hydroxide solution of 23°C for 60 seconds.

Also, the chemically amplified resist composition can give a line width difference between
5 resist top and resist bottom, of 10% or less, in a resist pattern of 0.12 micron formed; when the resist composition is coated on bare silicon to form a resist of 0.5 micron in thickness, a light of 193 nm emitted from an argon fluorine excimer laser is
10 applied to the resist at an exposure of 5 mJ/cm² or less through a mask having a pattern of line/space = 1/1 to project the pattern to the resist in 1/4 reduction, and the resulting resist is heat-treated at 120°C for 60 seconds and subjected to development
15 with a 2.38 mass % aqueous tetramethylammonium hydroxide solution of 23°C for 60 seconds.

Hereinafter, the present invention is described more specifically by producing the chemically amplified resist composition of the present invention.
20 In the following, "parts" refer to "parts by mass" unless otherwise specified, and commercial high-purity products were used for chemical reagents.

Properties of resins were measured as follows.

Weight-average molecular weight

25 Determined in terms of polymethyl methacrylate-

reduced weight-average molecular weight by gel permeation chromatography (GPC).

Average comonomer composition (mole %)
of copolymer

5 Determined by ^1H -NMR measurement. Deuterated chloroform or deuterated acetone was used as a solvent.

Resists were evaluated as follows.

Sensitivity

10 A resist composition solution was spin-coated on a silicon wafer and prebaked at 120°C for 60 seconds using a hot plate to form a resist film of 0.5 μm in thickness. Then, a mask having a pattern of line/space = 1/1 was projected to the resist film
15 in 1/4 reduction, using a KrF excimer laser beam aligner or an ArF excimer laser beam aligner. The resulting resist film was baked at 120°C for 60 seconds using a hot plate, after which the resist film was developed with a 2.38 mass % aqueous
20 tetramethylammonium hydroxide solution of 23°C, washed with pure water, and dried to form a resist pattern. An exposure capable of forming a line and space pattern (L/S = 1/1) at a line width of 1/1 was measured and taken as the sensitivity of the resist
25 composition solution used.

Threshold resolution

The minimum dimension (μm) of the resist pattern formed at the above exposure was taken as the threshold resolution of the resist composition

5 solution used.

Resist shape

Resist shape was evaluated according to any of the following three methods.

First method: Resist sectional shape was
10 observed using an electron microscope. A case of inferior sectional shape was rated as "X"; a case which had a good sectional shape and wherein there was little formation of sparingly soluble surface layer, was rated as "O"; and a case which had a
15 better sectional shape, wherein there was little film thinning, and whose sectional shape was close to a rectangle, was rated as "⊙". Further, the difference in line width (DD) between resist top and resist bottom in 0.12 micron pattern was calculated
20 from the following formula;

$$\text{DD}(\%) = \left[\frac{(\text{line width at top} - \text{line width at bottom})}{(\text{line width at bottom})} \right] \times 100.$$

Second method: Resist sectional shape was observed using an electron microscope. A case of
25 rectangular sectional shape was rated as "good"; a

case wherein there was formation of sparingly soluble surface layer, was rated as "T-top"; a case wherein the top (surface) became thinner, was rated as "tapered"; and a case wherein the film thickness
5 became smaller, was rated as "film thinning".

Resin 1

In a nitrogen atmosphere, 20.0 parts of 1,4-dioxane was fed into a flask provided with a nitrogen inlet tube, a stirrer, a condenser and a thermometer.
10 The temperature of the hot water bath was increased to 80°C with the flask contents being stirred. Into the flask was dropwise added, at a given rate in 6 hours, a monomer solution of a mixture with 29.3 parts of 2-methacryloyloxy-2-methyladamantane
15 (abbreviation: MADMA), 15.0 parts of p-hydroxystyrene (abbreviation: HS), 62.5 parts of 1,4-dioxane and 1.9 parts of azobisisobutyronitrile. Then, the temperature of 80°C was kept for 2 hours to give rise to a reaction. The reaction mixture was diluted to
20 about two-fold with tetrahydrofuran. The diluted solution was dropped into about ten-fold water with stirring, to obtain a white precipitate (resin 1). The precipitate was collected by filtration and dried under vacuum at 60°C for about 40 hours.

25 The thus-obtained resin 1 was measured for

properties. It had a weight-average molecular weight of 12,000 and a comonomer ratio of MAdMA/HS = 51/49 mole %.

Resin 2

5 Resin 2 was produced in the same manner as in the case of the resin 1 except that 29.3 parts of MAdMA was replaced by 22.0 parts of p-tert-butoxystyrene (abbreviation: PTBST, molecular weight: 176). The resin 2 had a weight-average molecular
10 weight of 12,000 and a comonomer ratio of PTBST/HS = 51/49 mole %.

Resin 3

 In a nitrogen atmosphere, 20.0 parts of 1,4-dioxane was fed into a flask provided with a nitrogen
15 inlet tube, a stirrer, a condenser and a thermometer. The temperature of the hot water bath was increased to 80°C with the flask contents being stirred. Into the flask was dropwise added, at a given rate in 6
20 hours, a monomer solution of a mixture with 29.3 parts of 2-methacryloyloxy-2-methyladamantane (abbreviation: MAdMA), 21.2 parts of β-methacryloyloxy-γ-butyrolactone (abbreviation: HGBMA), 62.5 parts of 1,4-dioxane and 1.9 parts of azobisisobutyronitrile. Then, the temperature of
25 80°C was kept for 2 hours to give rise to a reaction.

The reaction mixture was diluted to about two-fold with tetrahydrofuran. The diluted solution was dropped into about ten-fold methanol with stirring, to obtain a white precipitate (resin 3). The
5 precipitate was collected by filtration and dried under vacuum at 60°C for about 40 hours.

The thus-obtained resin 3 was measured for properties. It had a weight-average molecular weight of 11,000 and a comonomer ratio of MAdMA/HGBMA =
10 50/50 mole %.

Chemically amplified resist compositions

1 to 10

There were mixed, as shown in Table 1-1, 100 parts of a resin, 2 parts of triphenylsulfonium
15 triflate (as an agent generating an acid when irradiated with a light), 0.1 mole (per mole of the photo acid generator) of an amide derivative and 500 parts of propylene glycol monomethyl ether acetate (as a solvent), to form a uniform solution. The
20 solution was filtered through a membrane filter having a pore diameter of 0.1 μm , to produce chemically amplified resist compositions 1 to 10.

Resist patterns of the chemically amplified resist compositions 1, 2, 3, 7 and 9 were formed
25 using a KrF excimer laser beam aligner and evaluated.

The results are shown in Table 1-2.

Resist patterns of the chemically amplified resist compositions 4, 5, 6, 8 and 10 were formed using an ArF excimer laser beam aligner and evaluated.

5 The results are shown in Table 1-3.

It was appreciated from these evaluation results that by allowing a resist composition to contain an amine derivative having a particular skeleton, the resulting resist composition could have
10 a higher resolution without inviting a large reduction in sensitivity and showed a good resist shape.

Table 1-1

	Composition	Resin	Amine derivative
5	1	1	N-isopropylmethacrylamide
	2	1	N-cyclohexylformamide
	3	1	1-Cyclohexyl-2-pyrrolidinone
	4	3	N-isopropylmethacrylamide
	5	3	N-cyclohexylformamide
10	6	3	1-Cyclohexyl-2-pyrrolidinone
	7	1	No addition
	8	3	No addition
	9	1	N-phenyldiethanolamine
	10	3	2,6-Diisopropylaniline
15			

Table 1-2

	Composition	Sensitivity (mJ/cm ²)	Resolution (μm)	Resist shape
20	1	11.6	0.26	○
	2	10.2	0.25	⊙
	3	13.5	0.25	⊙
	7	10.1	0.35	X
	9	35.2	0.35	X

Table 1-3

	Composition	Sensitivity (mJ/cm ²)	Resolution (μm)	Resist shape	DD (%)
30	4	4.0	0.12	○	7
	5	3.6	0.12	⊙	4
	6	4.5	0.12	⊙	4
	8	3.6	0.16	X	16
35	10	25.6	0.17	X	25

Chemically amplified resist compositions

11 to 22

Chemically amplified resist compositions 11 to 22 were produced in the same manner as in the case of the chemically amplified resist compositions 1 to 10 except that the resins and amine derivatives shown in Table 2-1 were used. Incidentally, the conjugate acid of N-isopropylmethacrylamide had a pKa of -1.5, the conjugate acid of N-methylacetamide had a pKa of -0.42, the conjugate acid of ϵ -caprolactam had a pKa of -0.46, the conjugate acid of dimethylaminoethyl methacrylate had a pKa of 10, and the conjugate acid of cyanoethyl methacrylate had a pKa of -6.

Resist patterns of the chemically amplified resist compositions 11, 12, 13, 17, 18 and 19 were formed using a KrF excimer laser beam aligner and evaluated. The results are shown in Table 2-2.

Resist patterns of the chemically amplified resist compositions 14, 15, 16, 20, 21 and 22 were formed using an ArF excimer laser beam aligner and evaluated. The results are shown in Table 2-3.

It was appreciated from these evaluation results that by allowing a resist composition to contain an amine derivative having a particular basicity, the resulting resist composition could have

a higher resolution without inviting a large reduction in sensitivity and showed a good resist shape.

Table 2-1

	Composition	Resin	Amine derivative
5	11	2	N-isopropylmethacrylamide
	12	2	N-methylacetamide
	13	2	ϵ -caprolactam
	14	3	N-isopropylmethacrylamide
	15	3	N-methylacetamide
10	16	3	ϵ -caprolactam
	17	2	No addition
	18	2	Dimethylaminoethyl methacrylate
	19	2	Cyanoethyl methacrylate
	20	3	No addition
15	21	3	Dimethylaminoethyl methacrylate
	22	3	Cyanoethyl methacrylate

Table 2-2

	Composition	Sensitivity (mJ/cm ²)	Resolution (μ m)	Resist shape
20	11	11.2	0.25	Good
	12	12.2	0.26	Good
25	13	13.5	0.26	Good
	17	10.1	0.35	T-top
	18	35.2	0.35	Tapered
	19	11.0	0.35	T-top

30

Table 2-3

	Composition	Sensitivity (mJ/cm ²)	Resolution (μ m)	Resist shape
35	14	5.0	0.13	Good
	15	5.8	0.14	Good
	16	6.0	0.14	Good
	20	3.6	0.16	T-top
	21	21.2	0.19	Tapered
40	22	3.6	0.17	T-top

Chemically amplified resist compositions

23 to 34

Chemically amplified resist compositions 23 to 34 were produced in the same manner as in the case of the chemically amplified resist compositions 1 to 10 except that the resins and amine derivatives shown in Table 3-1 were used.

Incidentally, the Log P of N-isopropylmethacrylamide was 0.97, the Log P of 1-cyclohexyl-2-pyrrolidinone was 1.21, the Log P of N-cyclohexylformamide was 0.83, the Log P of N-acetylethanolamine was -1.24, and the Log P of 2-pyrrolidinone was -0.58. The water-octanol partition coefficient (Log P) shown here are water-octanol partition coefficients of Ghose, Pritchett and Crippen, calculated from RHF/STO-3G.

Resist patterns of the chemically amplified resist compositions 23, 24, 25, 29, 30 and 31 were formed using a KrF excimer laser beam aligner and evaluated. The results are shown in Table 3-2.

Resist patterns of the chemically amplified resist compositions 26, 27, 28, 32, 33 and 34 were formed using an ArF excimer laser beam aligner and evaluated. The results are shown in Table 3-3.

It was appreciated from these evaluation

results that by allowing a resist composition to contain an amine derivative having a particular polarity, the resulting resist composition could have a higher resolution without inviting a large
5 reduction in sensitivity and showed a good resist shape.

Table 3-1

	Composition	Resin	Amine derivative
5	23	2	N-isopropylmethacrylamide
	24	2	1-Cyclohexyl-2-pyrrolidinone
	25	2	N-cyclohexylformamide
	26	3	N-isopropylmethacrylamide
	27	3	1-Cyclohexyl-2-pyrrolidinone
10	28	3	N-cyclohexylformamide
	29	2	No addition
	30	2	N-acetylethanolamine
	31	2	2-Pyrrolidinone
15	32	3	No addition
	33	3	N-acetylethanolamine
	34	3	2-Pyrrolidinone

Table 3-2

	Composition	Sensitivity (mJ/cm ²)	Resolution (μm)	Resist shape
20	23	11.2	0.26	Good
	24	13.2	0.25	Good
25	25	13.0	0.25	Good
	29	10.1	0.35	T-top
	30	15.2	0.35	Film thinning
	31	13.5	0.35	Film thinning

30

Table 3-3

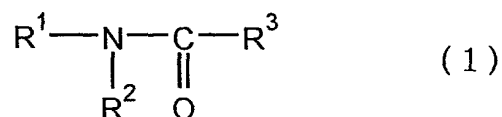
	Composition	Sensitivity (mJ/cm ²)	Resolution (μm)	Resist shape
35	26	5.0	0.14	Good
	27	5.8	0.13	Good
	28	5.5	0.13	Good
	32	3.6	0.16	T-top
	33	7.0	0.18	Film thinning
40	34	5.0	0.17	Film thinning

CLAIMS

1. A chemically amplified resist composition comprising:

- 5 a resin which becomes soluble in an aqueous alkali solution in the presence of an acid,
a photo acid generator, and
an amine derivative which shows, in water of 25°C, such a basicity as to form a conjugate acid and
10 has a medium polarity.

2. A chemically amplified resist composition according to Claim 1, wherein the amine derivative is an amide compound represented by the following
15 general formula (1):



(wherein R¹, R² and R³ are each independently hydrogen or an alkyl group having 1 to 30 carbon atoms).

- 20 3. A chemically amplified resist composition according to Claim 2, wherein in the general formula (1), at least two of R¹, R² and R³ bond to each other to form a cyclic skeleton.

4. A chemically amplified resist composition according to Claim 2, wherein in the general formula (1), at least one of R¹ and R² is a cyclic alkyl group having 3 to 30 carbon atoms.

5

5. A chemically amplified resist composition according to one of Claims 1 to 4, wherein the amine derivative is a basic compound which forms a conjugate acid having a pKa of -3 to 3, in water of

10 25°C.

6. A chemically amplified resist composition according to one of Claims 1 to 4, wherein the amine derivative is a basic compound which has such a polarity as to give a water-octanol partition coefficient (Log P) of 0 to 1.5 at 25°C.

15

7. A chemically amplified resist composition according to Claim 1, wherein the resin soluble in an aqueous alkali solution in the presence of an acid is a polymer comprising a (meth)acrylic acid ester monomer unit having an alicyclic skeleton, and a (meth)acrylic acid ester monomer unit having a lactone skeleton.

25

8. A chemically amplified resist composition according to Claim 7, wherein the (meth)acrylic acid ester monomer unit having the alicyclic skeleton is at least one kind selected from the group consisting of cyclohexyl (meth)acrylate, isobornyl (meth)acrylate, adamantyl (meth)acrylate, tricyclodecanyl (meth)acrylate, dicyclopentadienyl (meth)acrylate, and their derivatives formed by introducing a substituent onto the alicyclic ring of the monomer unit.

9. A chemically amplified resist composition according to Claim 7, wherein the (meth)acrylic acid ester monomer unit having the lactone skeleton is at least one kind selected from the group consisting of (meth)acrylates having a δ -valerolactone ring, (meth)acrylates having a γ -butyrolactone ring, and their derivatives formed by introducing a substituent onto the lactone ring of the monomer unit.

10. A chemically amplified resist composition which gives a threshold resolution of 0.15 micron or less, when the resist composition is coated on bare silicon to form a resist of 0.5 micron in thickness, a light of 193 nm emitted from an argon fluorine

excimer laser is applied to the resist at an exposure of 5 mJ/cm² or less through a mask having a pattern of line/space = 1/1 to project the pattern to the resist in 1/4 reduction, and the resulting resist is
5 heat-treated at 120°C for 60 seconds and subjected to development with a 2.38 mass % aqueous tetramethylammonium hydroxide solution of 23°C for 60 seconds.

10 11. A chemically amplified resist composition which gives a line width difference between resist top and resist bottom, of 10% or less, in a resist pattern of 0.12 micron formed,

when the resist composition is coated on bare
15 silicon to form a resist of 0.5 micron in thickness, a light of 193 nm emitted from an argon fluorine excimer laser is applied to the resist at an exposure of 5 mJ/cm² or less through a mask having a pattern of line/space = 1/1 to project the pattern to the
20 resist in 1/4 reduction, and the resulting resist is heat-treated at 120°C for 60 seconds and subjected to development with a 2.38 mass % aqueous tetramethylammonium hydroxide solution of 23°C for 60 seconds.

25

Declaration and Power of Attorney For Patent Application

特許出願宣言書及び委任状

Japanese Language Declaration

日本語宣言書

下記の氏名の発明者として、私は以下の通り宣言します。

As a below named inventor, I hereby declare that:

私の住所、私書箱、国籍は下記の私の氏名の後に記載された通りです。

My residence, post office address and citizenship are as stated next to my name.

下記の名称の発明に関して請求範囲に記載され、特許出願している発明内容について、私が最初かつ唯一の発明者（下記の氏名が一つの場合）もしくは最初かつ共同発明者（下記の名称が複数の場合）であると信じています。

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled.

CHEMICALLY AMPLIFIED RESIST
COMPOSITION

上記発明の明細書は、

- ☐ 本書に添付されています。
- ☐ ____月____日に提出され、米国出願番号または特許協定条約国際出願番号を____とし、
(該当する場合) ____に訂正されました。

the specification of which

- ☒ is attached hereto.
- ☒ was filed on July 11, 2000
as United States Application Number or
PCT International Application Number
PCT/JP00/04623 and was amended on
____ (if applicable).

私は、特許請求範囲を含む上記訂正後の明細書を検討し、内容を理解していることをここに表明します。

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

私は、連邦規則法典第37編第1条56項に定義されるとおり、特許資格の有無について重要な情報を開示する義務があることを認めます。

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, Section 1.56.

Japanese Language Declaration

(日本語宣言書)

私は、米国法典第35編119条 (a) - (d) 項又は365条 (b) 項に基づき下記の、米国以外の国の少なくとも一カ国を指定している特許協力条約365 (a) 項に基づく国際出願、又は外国での特許出願もしくは発明者証の出願についての外国優先権をここに主張するとともに、優先権を主張している、本出願の前に出願された特許または発明者証の外国出願を以下に、枠内をマークすることで、示しています。

Prior Foreign Application(s)

外国での先行出願

1911-198160	Japan
(Number) (番号)	(Country) (国名)
1911-199098	Japan
(Number) (番号)	(Country) (国名)
1911-199099	Japan
(Number) (番号)	(Country) (国名)
1911-230059	Japan
(Number) (番号)	(Country) (国名)
(Number) (番号)	(Country) (国名)
(Number) (番号)	(Country) (国名)

私は、第35編米国法典119条 (e) 項に基づいて下記の米国特許出願規定に記載された権利をここに主張いたします。

(Application No.) (出願番号)	(Filing Date) (出願日)
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(Application No.) (出願番号)	(Filing Date) (出願日)
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私は、私自信の知識に基づいて本宣言書で私が行なう表明が真実であり、かつ私の入手した情報と私の信じているところに基づく表明が全て真実であると信じていること、さらに故意になされた虚偽の表明及びそれと同等の行為は米国法典第18編第1001条に基づき、罰金または拘禁、もしくはその両方により処罰されること、そしてそのような故意による虚偽の声明を行なえば、出願した、又は既に許可された特許の有効性が失われることを認識し、よってここに上記のごとく宣誓を致します。

I hereby claim foreign priority under Title 35, United States Code, Section 119 (a)-(d) or 365(b) of any foreign application(s) for patent or inventor's certificate, or Section 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed.

Priority Claimed
優先権主張

12/07/1999	<input checked="" type="checkbox"/>	<input type="checkbox"/>
(Day/Month/Year Filed) (出願年月日)	Yes はい	No いいえ
13/07/1999	<input checked="" type="checkbox"/>	<input type="checkbox"/>
(Day/Month/Year Filed) (出願年月日)	Yes はい	No いいえ
13/07/1999	<input checked="" type="checkbox"/>	<input type="checkbox"/>
(Day/Month/Year Filed) (出願年月日)	Yes はい	No いいえ
16/08/1999	<input checked="" type="checkbox"/>	<input type="checkbox"/>
(Day/Month/Year Filed) (出願年月日)	Yes はい	No いいえ
(Day/Month/Year Filed) (出願年月日)	<input type="checkbox"/>	<input type="checkbox"/>
(Day/Month/Year Filed) (出願年月日)	Yes はい	No いいえ

I hereby claim the benefit under Title 35, United States Code, Section 119(e) of any United States provisional application(s) listed below.

(Application No.) (出願番号)	(Filing Date) (出願日)
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I hereby claim the benefit under Title 35, United States Code, Section 120 of any United States application(s), or Section 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of Title 35, United States Code Section 112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, Section 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of application.

(Status: Patented, Pending, Abandoned)
(現況: 特許許可済、係属中、放棄済)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Japanese Language Declaration
(日本語宣言書)

委任状：私は下記の発明者として、本出願に関する一切の手続きを米特許商標局に対して遂行する弁理士または代理人として、下記の者を指名いたします。
(弁護士、または代理人の指名及び登録番号を明記のこと)

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith: (list name and registration number)



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発明者の署名	日付	Inventor's signature	Tadayuki Fujiwara Dec. 27, 2001
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国籍		Citizenship	Japanese
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第二の共同発明者の氏名	200	Full name of second joint inventor, if any	Yukiya WAKISAKA
第二の共同発明者の署名	日付	Second joint Inventor's signature	Yukiya Wakisaka Dec. 27, 2001
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国籍		Citizenship	Japanese
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(第三以降の共同発明者についても同様に記載し、署名すること)

(Supply similar information and signature for third and subsequent joint inventors.)

Japanese Language Declaration

(日本語宣言書)

第三の共同発明者の氏名	300	Full name of third joint inventor, if any Masayuki TOOYAMA
第三の共同発明者の署名	日付	Third joint inventor's signature Masayuki Tooyama Date Dec. 27, 2001
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国籍		Citizenship
郵便の宛先		Post Office Address

第五の共同発明者の氏名		Full name of fifth joint inventor, if any
第五の共同発明者の署名	日付	Fifth joint inventor's signature Date
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国籍		Citizenship
郵便の宛先		Post Office Address

第六の共同発明者の氏名		Full name of sixth joint inventor, if any
第六の共同発明者の署名	日付	Sixth joint inventor's signature Date
住所		Residence
国籍		Citizenship
郵便の宛先		Post Office Address

(第六またはそれ以降の共同発明者に対しても同様な情報および署名を提供すること。)

(Supply similar information and signature for third and subsequent joint inventors.)